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Seasonal variation of resuspension-mediated aerobic release of phosphorus

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In shallow lakes, sediment resuspension can occur frequently. Therefore, the surface sediment is often well oxidized, and the effect of aerobic phosphorus release on internal nutrient loading can be substantial as compared with anoxic phosphorus release. The effect of resuspension on the aerobic release of phosphorus was studied in the field using experimental water columns. The study included three experiments that were conducted in May, August, and October in the shallow Kirkkojärvi basin of Lake Hiidenvesi. The concentrations of suspended solids (SS) and total phosphorus (TP) increased substantially due to the 10-min resuspension event in all the experiments. However, the concentration of soluble reactive phosphorus (SRP) was strongly affected only in August, when the high pH levels promoted SRP release by ligand-exchange reactions. In August, the amount of resuspended TP remaining in the water column 4 hours after the resuspension event equalled the external phosphorus loading of 13 days. Moreover, 46% of the TP increase was in the form of SRP and thus significantly affected the availability of phosphorus for phytoplankton growth. The results demonstrated that resuspension brings substantial amounts of soluble phosphorus into the water column, providing that it occurs during algal blooms when pH in the water column is high. The effect of sediment resuspension on the availability of phosphorus in the shallow Kirkkojärvi basin thus depends on conditions in the water column, which vary with the phase of the growing season.

Introduction

In many lakes, sediment resuspension has a significant effect on nutrient cycling. Especially in shallow waterbodies, resuspension-mediated internal loading often forms the main flux of nutrients into the water column (Kristensen *et al*. 1992, Niemistö and Horppila 2007). Sediment contains large pools of phosphorus and as phosphorus often acts as the limiting growth factor for phytoplankton in lakes, resuspension is of great importance in controlling the lake productivity (Boström *et al*. 1982, Kristensen *et al*. 1992). The effects of resuspension on the availability of phosphorus for algal growth are, however, complicated. Resuspended particles may release SRP (soluble reactive phosphorus), have no effect on SRP concentration, or adsorb SRP (Boström *et al*. 1988a, Søndergaard *et al*. 1992, Horppila and Nurminen 2001). It depends e.g. on the phosphorus concentration in the water and in the particles, whether phosphorus will be released or adsorbed (Søndergaard *et al*. 1992, Koski-Vähälä and Hartikainen 2000).

Phosphorus and its reactions in the sediment are often related to the chemistry of iron and redox potential. Numerous studies have demonstrated that low redox potential may lead to the release of iron-bound phosphorus to the overlying water (Mortimer 1941, 1942, Boström *et al*. 1982). However, in shallow lakes also aerobic release of phosphorus can be substantial (e.g. Golterman 1976, Søndergaard *et al*. 2003). For instance, at high pH phosphorus can be released from iron and aluminium oxides due to the ligand-exchange reactions (Hingston *et al*. 1967, Lijklema 1977, Koski-Vähälä and Hartikainen 2001). Sediment resuspension contributes to the release by transporting material to the water layers where pH is elevated due to primary production (Koski-Vähälä and Hartikainen 2001).

Previously, the effects of resuspension on the release of SRP have been studied mostly in the laboratory (e.g. Søndergaard *et al*. 1992, Reddy *et al*. 1996, Koski-Vähälä and Hartikainen 2000). Interpretation of laboratory results is, however, difficult. When sediment cores and water are transferred to the laboratory, their characteristics change and results may thus not be applicable to field conditions (Koski-Vähälä and Hartikainen 2000). Therefore, it is valuable to perform field studies where the water, sediment, and sediment-water interface are not disturbed before the experiments. In the present study, the aim was to determine the influence of resuspension on the aerobic release of phosphorus with field experiments. Koski-Vähälä and Hartikainen (2001) concluded that sediment resuspension will increase the concentration of SRP in the water column especially if it takes place during algal blooms and consequently at high pH. To examine the validity of this hypothesis, the present study was performed at different times of the growing season in the eutrophic Kirkkojärvi basin, where cyanobacterial blooms are annual phenomena (Tallberg *et al*. 1999, Tallberg and Horppila 2005). It was hypothesized that resuspension-mediated release of SRP would be more pronounced during summer when phytoplankton biomass is high than in spring or autumn when primary production is less intensive.

Material and methods

Study area

The study was performed in the shallow (mean depth 1.1 m, max. depth 3.5 m) Kirkkojärvi basin of Lake Hiidenvesi, which is situated in southern Finland (60°24´N, 24°18´E). Kirkkojärvi (area 1.6 km^2) is the most eutrophic basin of Lake Hiidenvesi. The summertime TP concentration varies between 80 and 120 μg l^{-1} and TN concentration between 1000 and 1500 μg l^{-1}. Due to resuspended sediments and runoff from agricultural areas, water turbidity is often high, varying from 20 to 70 NTU and Secchi depth usually remains below 0.5 m. To find more detailed information about Lake Hiidenvesi and the Kirkkojärvi basin see descriptions by Tallberg *et al*. (1999), Nurminen *et al*. (2001), and Niemistö and Horppila (2007).

Experimental setup and sampling

The effects of resuspension events were studied during three different periods of the ice-free season 2006. The experiments were conducted on 18 May, 2 August, and 10 October in the experimental columns that were open to the lake bottom and placed at 1 m depth. The height of each column was 1.3 m and the diameter 18.5 cm. Three columns were used as control units while in other three columns resuspension was conducted with a piston (Søndergaard *et al*. 1992). During the 10-min resuspension treatment, each column was mixed with few consecutive 10–15-sec bursts. A piston was moved for 10 min in the uppermost 50 cm of water according to the maximum wave heights usually occurring in Kirkkojärvi (Horppila and Nurminen 2001). The intensity of resuspension was evaluated with turbidity measurements. To be able to use turbidity as a measure of suspended solids, a linear regression model between turbidity and concentration of suspended solids was established using different concentrations of sediment from the Kirkkojärvi basin (SS = 1.5515 × Turbidity – 4.7178, R^2 = 0.9883, p < 0.0001, $F_{1,24}$ = 1942.84). In the experiments, the aim was to create resuspension strong enough to transport all potentially resuspending material into the water column and elevate the concentration of suspended solids to 200–300 mg l^{-1}, which is the level found in many shallow lakes after intensive resuspension events (Hamilton and Mitchell 1996, James *et al*. 2004).

Sampling was conducted from the treated columns and from the control columns before the induced resuspension, immediately after the mixing was stopped, and then 20, 40, 60, 90, 120, 180, and 240 minutes after the resuspension event. Samples were taken from 45 cm depth with a small plastic bottle. Turbidity, pH, water temperature, chlorophyll *a* (fluorescence) and the concentration of dissolved oxygen (DO) were measured with a YSI6600-sonde (YSI Incorporation, Yellow Springs, OH, USA). The water samples were stored on ice until they were transported and analysed in the laboratory. The concentration of TP was analysed from each sample according to the method of Koroleff (1979) and SRP according to the method of Murphy and Riley (1962). For the analysis of SRP, 50 ml of water from each sample was filtered in the field immediately after sampling through a membrane filter (Schleicher & Schuell, pore size 0.45 μm). To determine the concentration of chlorophyll *a* in the experimental units, a linear regression model between fluorescence measurements and concentration of chlorophyll *a* was established using chlorophyll *a* samples from Kirkkojärvi (measured spectrofotometrically after extraction with ethanol, Niemistö *et al*. 2009) in August and October (August: Chlorophyll *a* = 6.4768 × Fluorescence – 22.7530, R^2 = 0.6269, p < 0.0001, $F_{1,24}$ = 40.32; October: Chlorophyll *a* = 4.1015 × Fluorescence – 3.6351, R^2 = 0.7587, p < 0.0001, $F_{1,28}$ = 88.02). In May, no chlorophyll *a* values were calculated due to technical problems with the fluorescence sensor. In the beginning and at the end of the experiments, the water temperature, pH, chlorophyll *a*, and DO were measured also outside the columns to find out the possible effect of columns on these parameters. The differences in the TP and SRP concentrations, DO, pH and temperature between resuspension columns and control columns during the experiments were analysed with Repeated Measures ANOVA. Before the analyses, the normality of the datasets was verified with the Shapiro-Wilk test and data were log-transformed if necessary.

The flux of resuspending SRP and TP during the experiment was calculated according to the equation

$$P_{\text{flux}} = (C_{\text{t}} - C_0) \times V/A,$$

where P_{flux} = net phosphorus flux per m^2 of sediment, C_{t} = SRP or TP concentration in the water 10 min after the beginning of the experiment (immediately after the induced resuspension), C_0 = initial concentration of SRP or TP, V = volume of water in the water column, and A = sediment area in the column (e.g. Steinman *et al*. 2004). Additionally, to take into account the probably rapid sedimentation of resuspended coarse bottom material, P_{flux} was calculated also for the whole duration of the experiments (C_{t} = SRP or TP concentration 4 hours after the resuspension event).

Phosphorus fractionation

The different pools of P in the surface sediment of Kirkkojärvi were determined two times in the summer of 2007 to ascertain the seasonal development of these pools and thereby to aid in the interpretation of the experimental results. The responses of the different P pools to environmental factors may give valuable information when assessing the potential for internal P loading (Koski-Vähälä 2001). In May and August 2007, surface sediments (0–1 cm) from the location of the resuspension experiments were collected with a Kajak corer (Kajak *et al*. 1965) and the phosphorus content was fractioned according to the method of Chang and Jackson (1957) (modified by Hartikainen 1979). For the fractionation, 2 replicate samples were used and the sample volume was 8 ml. The fractionation procedure separates phosphorus to four fractions by sequential extractions with NH_4Cl, NH_4F, NaOH and H_2SO_4. NH_4Cl extracts labile P, NH_4F aluminium-related P (Al-P), NaOH iron-related P (Fe-P) and H_2SO_4 calcium-related P (Ca-P).

Results

Water temperature, pH and DO concentration

The water temperature in the experimental columns was 13.0–13.5 °C during the May experiments, 19.6–20.3 °C in August, and 10.5–10.9 °C in October. The concentration of dissolved oxygen varied between 6.5 and 11.5 mg l^{-1} in the different experiments, while water pH ranged from 7 to 8 in May and October and between 9.0 and 9.6 during the August experiment. In May and October, no statistical differences between the resuspension columns and the control columns in the average values of these parameters were found (Repeated Measures ANOVA: $p > 0.05$) (Table 1). In August, water temperature (Repeated Measures ANOVA: F_1 = 37.13, p = 0.003), DO concentration (Repeated Measures ANOVA: F_1 = 33.25, p = 0.0004), and water pH (Repeated Measures ANOVA: F_1 = 56.20, p < 0.0001) were on average significantly lower in the resuspension columns than in the control columns (Table 1). No difference between the control columns and the lake water outside the columns was detected.

Concentrations of SS, TP, SRP and chlorophyll *a*

Due to the resuspension treatment, the concentration of SS was substantially elevated from the initial level in each of the three experiments (May: from 20 to 217 mg l^{-1}; August: from 58 to 316 mg l^{-1}; October: from 29 to 390 mg l^{-1}) (Fig. 1). Thereafter, the SS concentration decreased constantly and at the end of the experiment it was 46 mg l^{-1} in May, 81.1 mg l^{-1} in August, and 62.7 mg l^{-1} in October (Fig. 1). In the control units, the concentration of SS remained at the initial level throughout the experiments (Fig. 1).

The concentration of TP closely followed the pattern of SS in all the experiments. After the resuspension event, it increased steeply from the initial level (May: from 61 to 249 μg l^{-1}; August: from 246 to 529 μg l^{-1}; October: from 88 to 533 μg l^{-1}). Similar to SS, the concentrations of TP decreased rapidly after the treatment and at the end of the experiments the average concentration was 82 μg l^{-1} in May, 277 μg l^{-1} in August, and 126 μg l^{-1} in October (Fig. 2). In the control units, the concentration of TP did not change during the experiments (Fig. 2). The difference between the treated units and the control units was significant in all the three experiments (Table 2). In May, the net flux of TP into the water column was 188 mg m^{-2} after 10 min mixing and 21 mg m^{-2} after 4 hours. In August, the flux was 283 mg m^{-2} in 10 minutes and 31 mg m^{-2} in 4 hours. In October, the immediate flux was 445 mg m^{-2} and the 4 hour net flux 38 mg m^{-2}. In the control columns, no net TP flux into the water column was detected after 10 min resuspension or after 4 hours in any of the experiments.

The concentration of SRP in the treated columns varied between 7 and 12 μg l^{-1} during the May experiment. The immediate flux of SRP into the water due to the resuspension treatment was < 1 mg m^{-2} and SRP concentration remained

Table 1. The average values of water temperature, pH and concentration of dissolved oxygen (DO) in the experimental columns during the three different experiments.

	18 May		2 August		10 October	
	Resuspension columns	Control columns	Resuspension columns	Control columns	Resuspension columns	Control columns
Temp. (°C)	13.1	13.5	19.8	20.1	10.7	10.7
pH	7.5	7.5	9.1	9.4	7.8	7.7
DO (mg l^{-1})	11.0	11.2	6.9	7.5	8.1	8.0

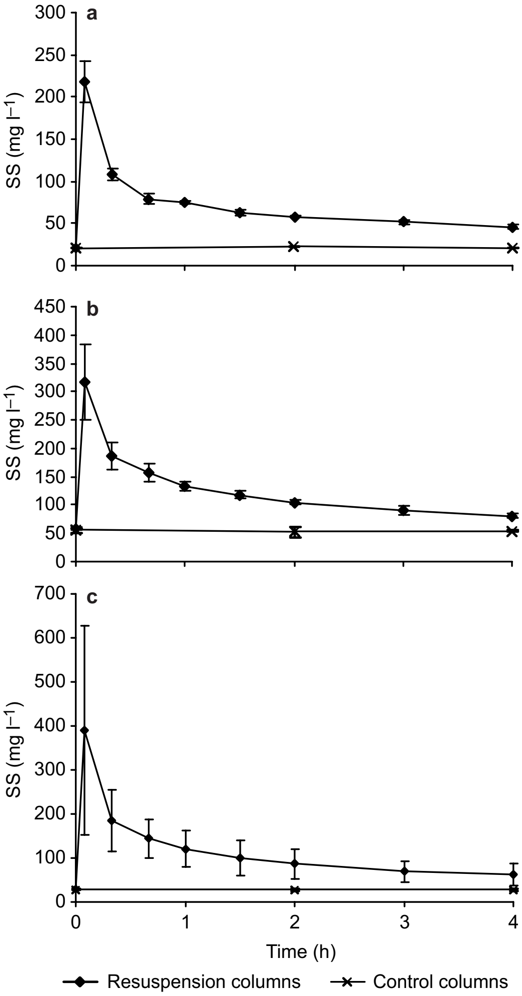

Fig. 1. Changes in concentration of suspended solids during the experiments (**a**) in May, (**b**) August and (**c**) October (± 95% confidence limits).

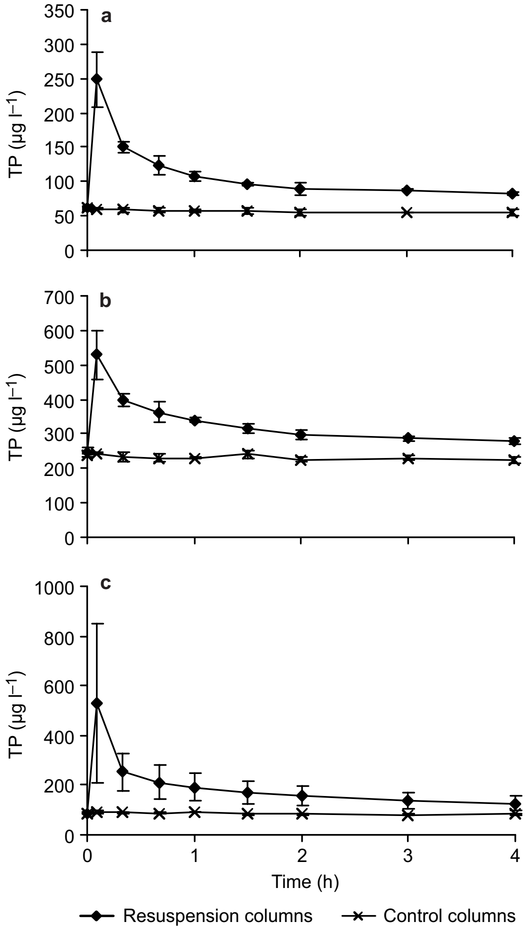

Fig. 2. Changes in total phosphorus concentration during the experiment in (**a**) May, (**b**) August and (**c**) October (± 95% confidence limits).

Table 2. Results from the analyses of variance for repeated measurements for the effects of resuspension treatment on the concentration of TP and SRP.

		Treatment			Time			Interaction		
		df	*F*	*p*	df	*F*	*p*	df	*F*	*p*
TP	18 May	1	1503.26	< 0.0001	8	76.65	< 0.0001	8	68.56	< 0.0001
	2 August	1	1002.21	< 0.0001	8	52.91	< 0.0001	8	41.96	< 0.0001
	10 October	1	600.88	< 0.0001	8	23.11	< 0.0001	8	26.19	< 0.0001
SRP	18 May	1	9.15	0.0049	8	2.93	0.0142	8	0.42	0.8989
	2 August	1	1338.70	< 0.0001	8	10.72	< 0.0001	8	27.56	< 0.0001
	10 October	1	2.95	< 0.0956	8	0.99	< 0.4643	8	1.05	0.4209

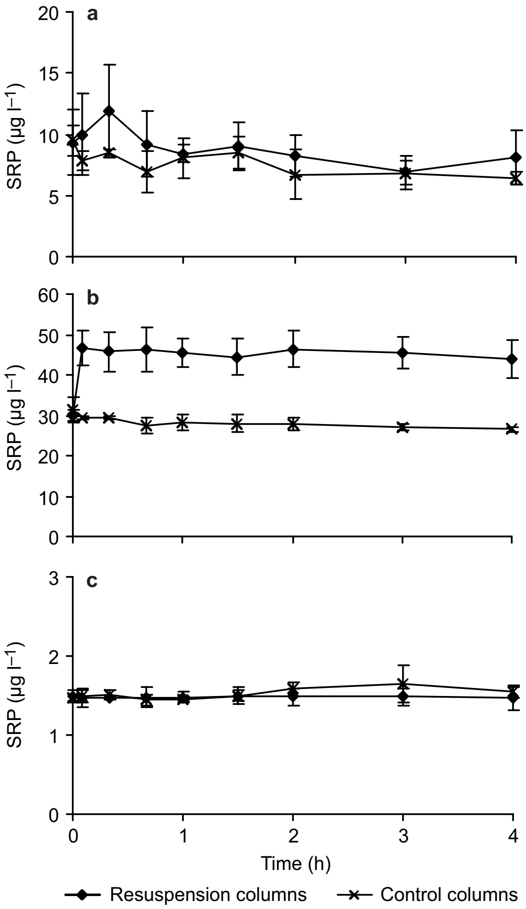

Fig. 3. Changes in SRP concentration during the experiments in (**a**) May, (**b**) August and (**c**) October (± 95% confidence limits).

slightly but significantly higher in the resuspension columns than in the control columns (Fig. 3 and Table 2). During the August experiment, the average concentration of SRP increased after the mixing from 30 μg l^{-1} to 47 μg l^{-1} and remained at a significantly higher level than in the control units (Fig. 3 and Table 2). The flux of SRP from the sediment into the water column caused by the treatment was 17 mg m^{-2}, 14 mg m^{-2} of which remained in the water column after 4 hours. SRP constituted 46% of TP flux. In October, the concentration of SRP was low (1.5–1.6 μg l^{-1}) (Fig. 3 and Table 2). Resuspension did not induce any net flux of SRP into the water column. In the control units, the concentration of SRP remained at the initial level throughout all the experiments (Fig. 3).

In the experimental columns in August, the initial concentration of chlorophyll *a* in the resuspension columns was 127 μg l^{-1} and after the mixing it increased to 184 μg l^{-1}. After two hours, the chlorophyll *a* concentration had decreased to 144 μg l^{-1} and remained at that level, being 142 μg l^{-1} at the end of the experiment. In the control columns, chlorophyll *a* concentration stayed between 125–132 μg l^{-1} throughout the experiment. In October, the development of the chlorophyll *a* concentration was similar that in August, although the values were lower. The concentration increased from the initial value of 24 μg l^{-1} to 55 μg l^{-1} after the resuspension and decreased thereafter being 32 μg l^{-1} at the end of the experiment. In the control columns, the chlorophyll *a* concentration remained below 30 μg l^{-1} throughout the experiment.

Phosphorus fractionation

The results of the fractionation of phosphorus in the surface sediment showed that from May to August the Al-P fraction decreased from 39.6 mg kg^{-1} (7.8% of total fractionable P [TFP]) to 25.5 mg kg^{-1} (5.3% of TFP) and the Fe-P fraction from 145.4 mg kg^{-1} (28.8% of TFP) to 90.6 mg kg^{-1} (18.9% of TFP). The fraction of labile phosphorus increased from 1.2 mg kg^{-1} (0.2% of TFP) to 4.2 mg kg^{-1} (0.9% of TFP) and the fraction of calcium bound P from 319.0 (63% of TFP) to 358.2 (75% of TFP) (Fig. 4).

Discussion

Aerobic release of phosphorus

As expected, the concentration of TP increased in the treated columns along with the SS concentration (Kristensen *et al*. 1992, Søndergaard *et al*. 1992), while the relationship between the SS and SRP concentrations was more complicated. Previous studies have shown that although resuspension increases the concentration of TP, it does not necessarily affect the concentration of SRP (Peters and Cattaneo 1984, Horppila and Nurminen 2001). The present study demonstrated that in a given lake the effect of resuspension on the SRP concentration in the water was dependent on the phase of the growing season. In October, resuspension had no effect on the SRP concentration, in May SRP in the water column increased slightly, and in August the effect of resuspension on SRP was strong.

The greatest differences in the environmental conditions between the August experiment and the other two periods occurred in water temperature and pH, although in August the mixing expectedly decreased those variables as well as the concentration of DO. In August, enhanced mineralization of organic matter due to high water temperature was probably the reason for the high initial concentration of SRP in the water column (Jensen and Andersen 1992), whereas the high pH was the main factor that contributed to the SRP release. Particulate phosphorus may become available due to ligand-exchange reactions especially in eutrophic waters, where primary production elevates pH during algal blooms (Drake and Heaney 1987, Boström *et al.* 1988b). In Kirkkojärvi, cyanobacterial blooms (e.g. *Anabaena flos-aquae*) occurred during the experiment in August (Ranta *et al.* 2007), as indicated by the high initial chlorophyll *a* concentration. During the August experiment, pH was on average 9.2, which is in the range where the highest net release of phosphorus occurs (Andersen 1975). At such a pH level, the net release of phosphorus is substantially higher than at pH 8, which was the pH level during the experiments in May and October (Van Hullebusch *et al.* 2003, Christophoridis and Fytianos 2006). The ligand-exchange reactions occur on both iron and aluminium oxides and phosphorus related to these fractions is susceptible to pH changes (e.g. Lijklema 1980, Boström *et al.* 1988b). Partly, the increase in the SRP concentration in August as well as in May could have resulted from the dissolving of the labile P fraction. However, the ligand exchange reactions played an important role already earlier in the summer. The fractions of Al-P and Fe-P in the sediment decreased and the fractions of labile P and Ca-P increased between May and August, supporting the conclusion that P was mainly released from Al- and Fe-hydroxides as a result of high pH during summer. A fraction of the released phosphorus may stay liberated in the water, while some part may be moved to fractions of labile P and Ca-P. The pool of labile P, which partly represents the loosely adsorbed organic P, is known to increase in the course of the summer due to the increasing deposit of newly produced material (Søndergaard 1989). The precipitation of P as hydroxyapatite at high pH (9–11) may increase the pool of Ca-bound phosphorus (Andersen 1975). Major part of the increase in the SRP concentration in May was probably also due to ligand exchange reactions, which can be accelerated by degradation of biogenic Si (silicon) after the spring diatom bloom. Large additions of Si may affect the release of P even without the increase in pH and this has been observed in the experiments conducted with the sediment of Lake Hiidenvesi (Koski-Vähälä *et al.* 2001, Tallberg and Koski-Vähälä 2001).

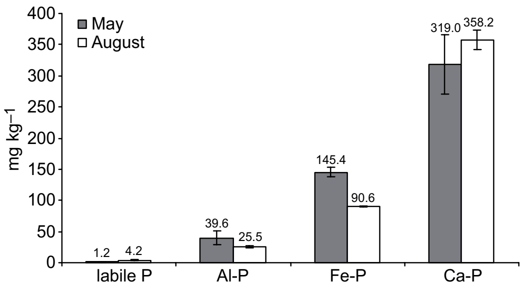

Fig. 4. Different phosphorus pools in May and August 2007 in the Kirkkojärvi basin (± 95% confidence limits).

When the pH in the water is high, it will also raise the pH of the surface sediment (Søndergaard 1990). Therefore, it is possible that part of the phosphorus being released will be already in the sediment pore water and resuspension will merely be the mechanism that transports it to the water column. However, the pore water concentration should be unlikely high to be able to considerably increase the concentration of SRP in the water column (Søndergaard *et al.* 1992, Reddy *et al.* 1996). The highest concentrations observed in the sediment pore water of Kirkkojärvi have been 40 μg l^{-1} (J. Niemistö unpubl. data). The concentration should be higher than 1000 μg l^{-1} to explain the SRP increase observed in the August experiment. The rapidly increased chlorophyll *a* concentration in the resuspension columns after the mixing was due to resuspended phytoplankton (Carrick *et al.* 1993, Schelske *et al*. 1995). Since resuspended phytoplankton may photosynthesize at rates similar to surface populations (Carrick *et al*. 1993), they probably attenuated the SRP increment in the resuspension columns.

Resuspension-mediated phosphorus fluxes

Due to the low mean depth, most of the bottom area of Kirkkojärvi is susceptible to intensive resuspension and in the open water area (excluding areas covered by macrophytes) the rate of resuspension shows little spatial variation (Niemistö *et al*. 2008). Calculated for the whole open water area of the Kirkkojärvi basin (outside the macrophyte stands, water depth > 0.7 m, area 98 ha) the internal TP loading caused by a single resuspension event, assuming it was of similar magnitude to the experimental manipulation, was 180 kg in May, 270 kg in August, and 445 kg in October. Taking into account the rapid sedimentation of the resuspended material, the amount of TP remaining in the water column after 4 hours was 20.2 kg in May, 29.6 kg in August, and 36.8 kg in October. In areas shallower than this, macrophyte vegetation has significant effects on resuspension and nutrient dynamics and thus results of the present study are not applicable there (Horppila and Nurminen 2003, 2005). The external TP loading to Kirkkojärvi in 2006 was 10.9 kg d^{-1} in May, 2.2 kg d^{-1} in August, and 3.6 kg d^{-1} in October 2006 (Ranta *et al*. 2007). Excluding the rapidly sedimented material, the internal phosphorus loading caused by one resuspension event of similar magnitude to the experimental manipulation thus corresponded to the external load of 2 days in May, 13 days in August, and 10 days in October. Resuspension was thus of importance especially in late summer, when the water discharge from the drainage area of the lake was low. Moreover, the fact that 46% of the resuspended TP was in a soluble form emphasized the ecological importance of resuspension in late summer. The majority of the exchange reactions are known to take place within a few minutes (House *et al*. 1995). Therefore, our 10 minutes resuspension treatment was long enough to cause a major effect for P liberation. The estimated resuspension-mediated SRP flux (17 mg m^{-2} in 10 minutes) was in agreement with the studies by Reddy *et al*. (1996), who found a SRP net flux of 3.3 mg m^{-2} h^{-1}, almost all of which occurred during the first 15 minutes of resuspension. Søndergaard *et al*. (1992) concluded that a typical resuspension event could release as much as 150 mg SRP m^{-2}, but the duration of their resuspension treatment was several hours and the experiments were conducted with a sediment having a P content 2–3 times higher than in Kirkkojärvi (Horppila and Nurminen 2001). In Kirkkojärvi, the resuspension-induced SRP pulses are of importance, because the concentration of SRP in late summer is often < 10 μg l^{-1} due to low external loading and intensive assimilation by phytoplankton (Horppila and Nurminen 2001).

Conclusions

The concentrations of SS and TP increased substantially due to the resuspension treatment in May, August and October. However, the concentration of SRP was strongly affected only in August, when the high pH levels promoted SRP release by ligand exchange reactions.

In August, the amount of resuspended TP remaining in the water column in the end of the experiment equalled the external phosphorus loading of 13 days. Moreover, 46% of the TP increase was in the form of SRP and thus significantly affected the availability of phosphorus for phytoplankton growth.

The results demonstrated that resuspension brings substantial amounts of soluble phosphorus into the water column, providing that it occurs during algal blooms when pH in the water column is high. The effect of sediment resuspension on the availability of phosphorus in the shallow Kirkkojärvi basin thus depends on conditions in the water column, which vary with the phase of the growing season.

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